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13. ABSTRACT *(Maximum 200 Words)*

This project explored linear and non-linear optical structure-property relationships for Pt-acetylide oligomers and polymers. These materials show promise for application in laser protection via the reverse saturable absorption (RSA) mechanism. This basic science program had the following primary objectives: 1) Chemical synthesis and purification of new pi-conjugated Pt-acetylide oligomers and polymers. 2) Characterization of the ground and excited state properties of the new materials, with emphasis placed on measurement of parameters that are important to reverse saturable absorption. These parameters include ground state absorption spectra, singlet-triplet intersystem crossing yields, triplet excited state cross sections, and triplet excited state quenching via triplet-triplet annihilation. 3) Evaluate new materials for application as reverse saturable absorbers. The project also explored other key issues, including tuning the spectral region where the ground state and triplet excited states absorb for series of structurally-related Pt-acetylide materials, development of materials that are liquids at ambient temperature, and study of triplet excited state quenching in the solid state.

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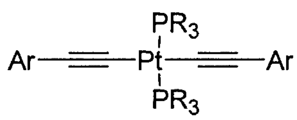
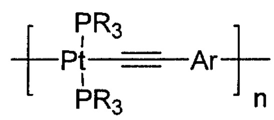
PI: Kirk S. Schanze, Department of Chemistry, University of Florida

During the past three years our group carried out a research program that investigated the photophysics and non-linear absorption properties of π-conjugated platinum-acetylide oligomers and polymers (Scheme 1).[1-6] The photophysical properties of these materials are dominated by long-lived, strongly absorbing triplet excited states. Due to the strong triplet excited state absorption, Pt-acetylides display non-linear absorption via the reverse saturable absorption (RSA) mechanism. As a result, this class of organometallic compounds has considerable potential for optical limiting applications.[7-9] Our research program on Pt-acetylides was carried out in close coordination with the Agile Limiters group at the Air Force Research Laboratory (AFRL/MLPJ). The AFRL/MLPJ group has an ongoing program that is focused on the development of organometallic materials for non-linear absorption applications, and the results from our basic science effort are helpful to them as they seek to design materials and systems that are optimized for specific applications.

Scheme 1



Pt-acetylide oligomer



Pt-acetylide polymer

This was a basic science program that had the following primary objectives: 1) Chemical synthesis and purification of new π-conjugated Pt-acetylide oligomers and polymers. 2) Characterization of the ground and excited state properties of the new materials, with emphasis placed on measurement of parameters that are important to reverse saturable absorption. These parameters include ground state absorption spectra, singlet-triplet intersystem crossing yields, triplet excited state cross sections, and triplet excited state quenching via triplet-triplet annihilation. 3) Evaluate new materials for application as reverse saturable absorbers. The project also explored other key issues, including tuning the spectral region where the ground state and triplet excited states absorb for series of structurally-related Pt-acetylide materials, development of materials that are liquids at ambient temperature, and study of triplet excited state quenching in the solid state. Detailed accounts of much of the prior work has been reported in several published manuscripts[1-6] and in annual progress reports. Here we summarize key findings that are not available in the published work.

A. Photophysics and Materials Properties of Liquid Platinum Acetylides. The non-linear response of a material is directly proportional to the chromophore density. As a result, in order to optimize the response of reverse saturable absorbing materials it is necessary to use very concentrated solutions or even use the materials in the pure form. Both of these approaches are facilitated by the preparation of materials that are liquids at ambient temperature.

On the basis of prior work by the AFRL/MLPJ group which demonstrated that incorporation of long alkyl chain phosphine ligands into Pt-acetylides affords materials that are liquids at ambient temperature,[10] we designed and synthesized the series of Pt-acetylide oligomers shown in Scheme 2. These oligomers feature $P(C_8H_{15})_3$ ligands that disrupt crystallization of the pure materials. As shown below, the oligothiophene chromophores impart strong ground state absorption and a wavelength tunable, triplet excited state absorption. As expected, the oligomers are liquids at ambient temperature (Figure 1), and differential scanning calorimetry (carried out by Dr. Thomas Cooper at AFRL) shows that the oligomers exhibit glass transition temperatures in the range -60 to -70 °C.

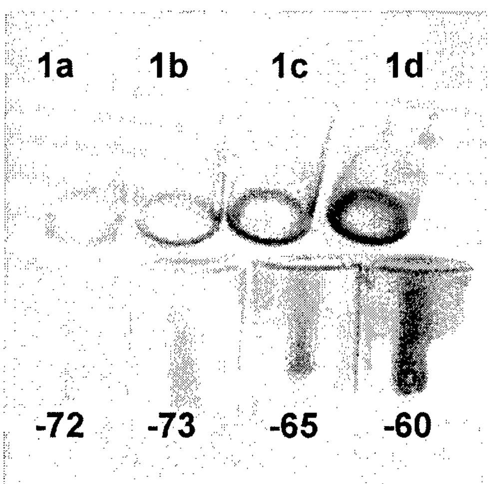
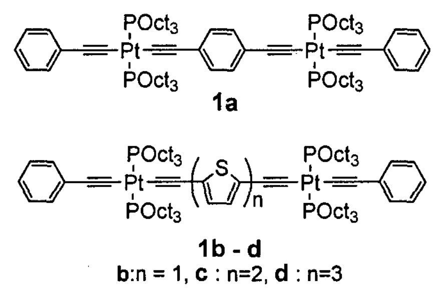


Figure 1. Vials containing liquid Pt-acetylides **1a** – **1d**. Numbers at bottom of photograph show glass transition temperatures in °C.

Scheme 2



Nanosecond transient absorption experiments were carried out on the oligomers in dilute solution and as pure liquids. As shown in Figure 2, each of the oligomers displays strong triplet-triplet absorption in the visible region, and the λ_{max} of the transient absorption red-shifts with increasing length of the oligothiophene chromophore. Transient absorption experiments carried out on the pure liquids (as thin films) show that the triplet-triplet absorption spectra are similar in bandshape and λ_{max} compared to those for the materials in dilute solution. However, despite the similarity of the triplet-triplet spectra for the pure liquids and dilute solutions, the triplet states decay considerably more rapidly in the pure films (see Figure 2). Although this effect was not explored in detail, the more rapid decay is believed to arise due to triplet-triplet annihilation and self-quenching.

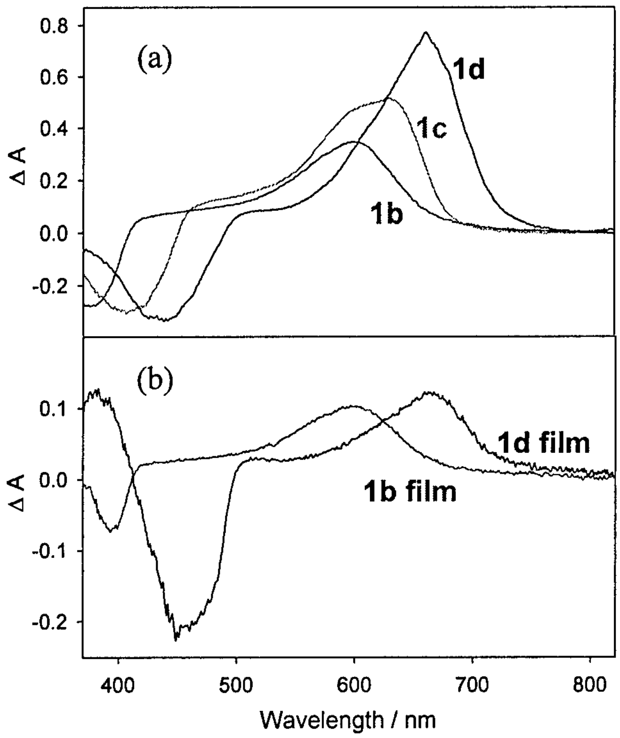
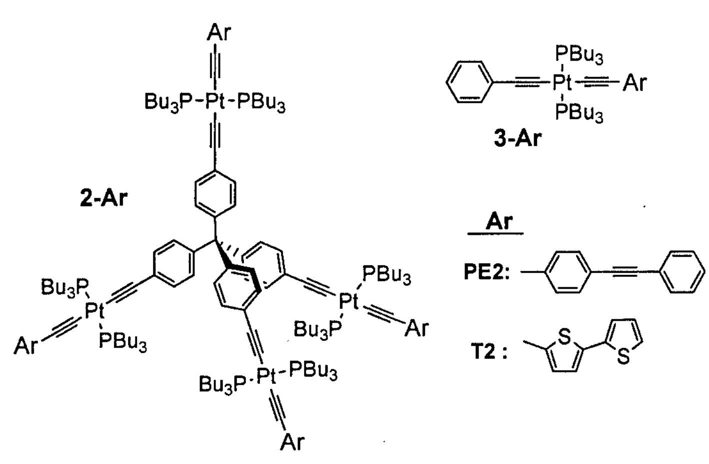


Figure 2. Transient absorption difference spectra of (a) **1b**, $\tau = 9.8$ μs; **1c**, $\tau = 4.5$ μs; and **1d**, $\tau = 4.4$ μs in degassed THF solution following 355 nm pulsed excitation. (b) Transient absorption spectra of **1b** film $\tau = 1.8$ μs; and **1d** film $\tau = 350$ ns following 355 nm pulsed excitation.

B. Triplet-Triplet Annihilation in Multi-Chromophore Pt-Acetylide Oligomers. In order for Pt-acetylide materials to be useful in non-linear absorption applications, the excited state properties of the materials in the solid state are important. Since inter-chain interactions have been shown to have a strong influence on properties of singlet excited states of organic materials in the solid state,[11-14] a significant component of our work on Pt-acetylides has been to investigate how inter-chain interactions influence the properties of the triplet excited state in the organometallic materials. In one line of investigation a series of tetrahedral-shaped Pt-acetylide oligomers were designed with the objective to minimize inter-chain contacts that are favored in the crystalline state (Scheme 3). This work was inspired by a recent investigation by Bazan and co-workers who showed that oligo(phenylene vinylene)s constructed around a tetrahedral core were amorphous solids with relatively high glass transition temperatures.[15]

An important effect that is relevant to the non-linear absorption properties of Pt-acetylide materials was discovered while examining the transient absorption spectroscopy of the tetrameric oligomers **2-Ar** and the corresponding monomeric model oligomers, **3-Ar**. Near-UV excitation of dilute THF solutions of these oligomers produces a long-lived triplet excited state that can be detected by transient absorption in the 500 – 700 nm region. The surprising effect uncovered in these experiments is that even though the samples have matched optical density at the laser excitation wavelength, the tetrameric oligomers **2-Ar** give rise to a significantly weaker transient absorption than the corresponding monomers, **3-Ar**.

Scheme 3



This effect was investigated more carefully by an experiment where the transient absorption (ΔA) was monitored as a function of laser fluence for solutions of the oligomers having matched optical density at the laser excitation wavelength. The results for **2-T2** and **3-T2** are shown in Figure 3a. As can be seen from this figure, at low laser fluence (< 4 mj-cm^{-2}) the plots are co-linear; however, at higher laser fluence the two plots deviate markedly-- the transient absorption of **3-T2** continues to increase while that for tetramer **2-T2** saturates. At the highest fluence examined ($\approx$ 60 mj-cm^{-2}), the ratio of the ΔA_{530} signal is approximately 4:1, which indicates at saturation the density of excited chromophores for the tetramer is one-fourth that which can be obtained for the corresponding monomer.

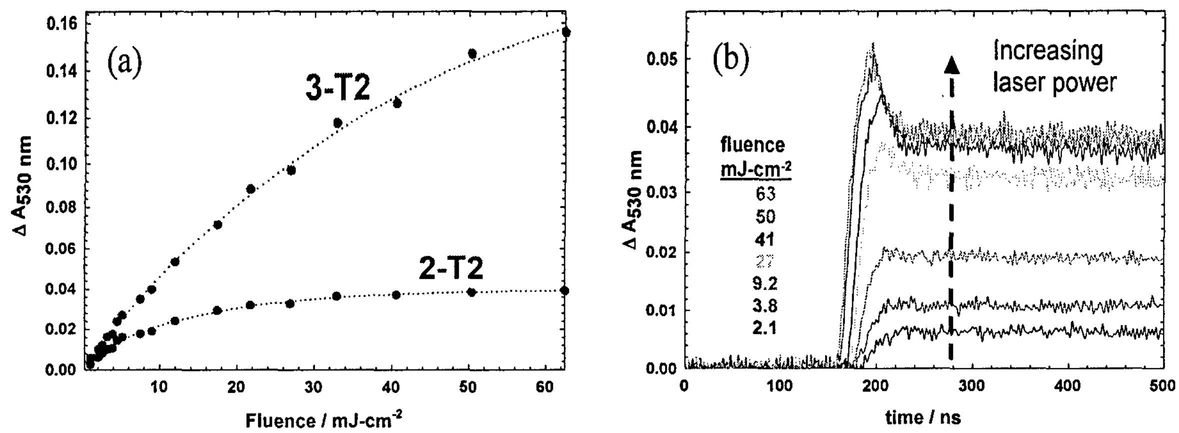


Figure 3. (a) Transient absorption signal intensity dependence at 530 nm for various laser fluence following 355 nm pulsed excitation for **2-T2** (red) and **3-T2** (green). (b) Temporal dependence of transient absorption of **2-T2** at early times following 10 ns excitation for various laser powers.

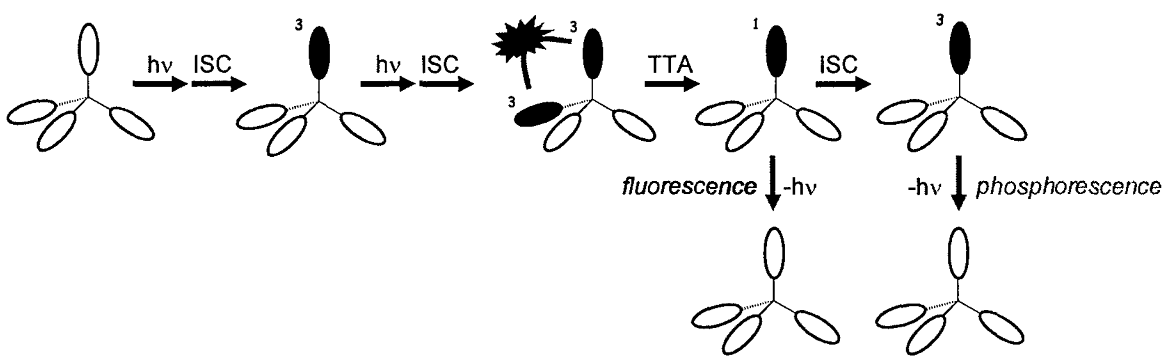


Figure 4. Illustration of triplet-triplet annihilation. The multi-chromophoric molecule is first doubly-excited, followed by TTA. This results in a singlet state that can either fluoresce or undergo ISC to form a triplet which can phosphoresce.

This effect is believed to arise because intramolecular triplet-triplet (T-T) annihilation (TTA) is an important process in the tetramers at high laser fluence. The cartoon shown in

Figure 4 qualitatively illustrates how this effect arises. At sufficiently high laser fluence, sequential, multi-photon excitation of a tetramer generates a single molecule containing two triplet-excited Pt-acetylide chromophores. Due to the close spatial proximity of the Pt-acetylide chromophores in **2-Ar**, intramolecular TTA is rapid (nanosecond timescale) and leads to the conversion of the two triplet excited chromophores into one singlet excited state and one ground state. Evidence for the rapid TTA process can be seen in the transient absorption traces shown in Figure 3b, where there is a fast triplet decay component seen at high laser excitation fluence. The consequence of this process is that at high laser fluence saturation of the sample occurs when only one Pt-acetylide chromophore per molecule is photoexcited. Additional evidence supporting the TTA mechanism has been obtained in transient absorption experiments carried out on a faster timescale, as well as in studies that explored the laser fluence dependence of the fluorescence:phosphorescence intensity ratio in **2-T2** and **3-T2**.

While the effect of intramolecular TTA in the tetrameric oligomers is interesting from a fundamental standpoint, we also believe that it has significant implications for the design and application of chromophore systems that give rise to non-linear absorption via the reverse saturable absorption (RSA) mechanism. Specifically, our results indicate that in systems containing multiple chromophores in close proximity (i.e., dendrimers or oligomers) TTA will become an important pathway which leads to rapid excited state deactivation. This will limit the excited state population that can be produced during long pulse excitation. Because the optical limiting response via RSA is linearly proportional to the excited state population,[16] efficient TTA will lead to reduced RSA response from the material.

C. Organometallic Chromophores for Dual Mode Non-Linear Absorption. In a recent series of synthetic and photophysical studies, we have designed and characterized a novel set of organometallic chromophores that exhibit efficient non-linear absorption via two mechanisms. Figure 5a illustrates the general concept that is being followed in this line of investigation.

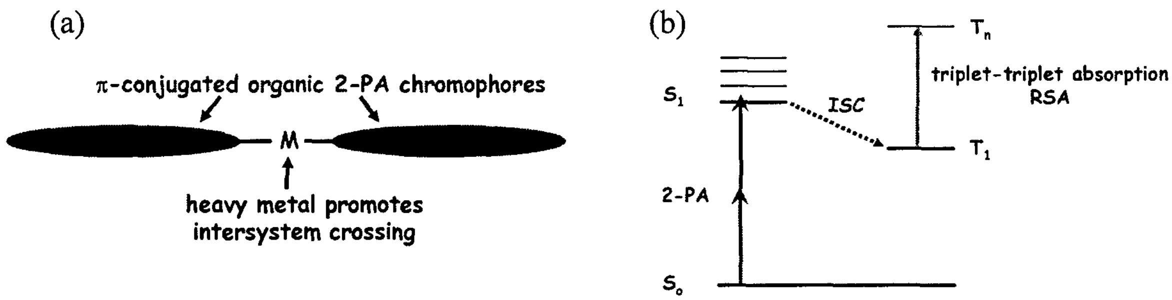


Figure 5. (a) Illustration of an organometallic chromophore for dual mode non-linear absorption. (b) Jablonski diagram showing dual mode non-linear absorption via two-photon absorption and reverse saturable absorption.

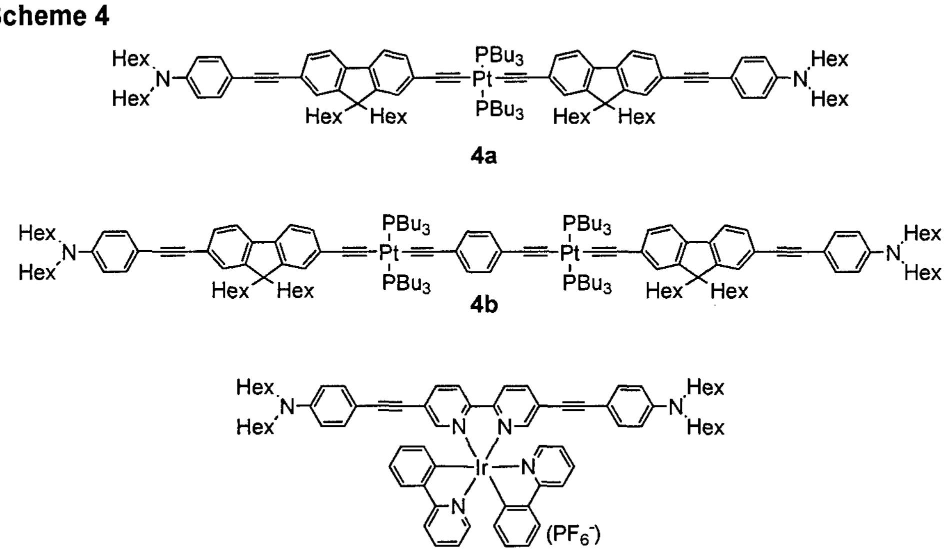
Specifically, we seek to prepare organometallic oligomers in which π-conjugated chromophores with large two-photon absorption (TPA) cross sections (σ_2') are strongly coupled to a transition metal chromophore that promotes intersystem crossing. As shown in the accompanying Jablonski diagram in Figure 5b, these organometallic oligomers have the potential to exhibit non-linear absorption and optical limiting by two mechanisms. First, due to the large σ_2' of the π-

conjugated chromophores, the oligomers can be excited into the first singlet excited state (S_1) by TPA. Second, due to the influence of the transition metal, rapid singlet-triplet intersystem crossing occurs ($S_1 \rightarrow T_1$), efficiently producing the triplet excited state. Due to the large cross section for the triplet-triplet absorption (σ_{TT}), the chromophores are anticipated to exhibit non-linear absorption via RSA.

While the organometallic TPA/RSA non-linear absorption chromophores are of fundamental interest, they also have considerable potential for application as optical limiting materials for several reasons. First, the materials will exhibit broad-timescale optical limiting behavior. Specifically, the chromophores will exhibit instantaneous limiting response for short timescale pulses (femtosecond/picosecond) by the TPA mechanism.[17-20] In addition, due to the long lifetime of the triplet excited state, the chromophores will also limit long laser pulses (nanosecond/microsecond) via reverse saturable absorption.[16] Second, since the primary mechanism for excitation is two-photon absorption, the materials are optically transparent at low light intensity in the spectral region where they are active at non-linear absorption.

In efforts carried out to date we have explored the properties of the series of three oligomers shown in Scheme 4. Each of these oligomers incorporates a heavy metal center into a donor-π-donor (D-π-D) type π-conjugated oligomer. On the basis of previous work carried out at AFRL and by other groups, the D-π-D chromophore systems are anticipated to exhibit large two-photon absorption cross sections ($\sigma_2' > 100$ GM, 1 GM = 10^{-50} cm^4-s-photon^{-1}-molecule^{-1}).[21-23] Platinum and iridium have the largest spin-orbit coupling constants of all the transition metals,[24] and consequently they are anticipated to give rise to high triplet yields via fast intersystem crossing.

Scheme 4



A series of investigations have been carried out to characterize the photophysics of the Pt(II) and Ir(III) complexes under conditions of one and two-photon excitation. The results clearly show that: 1) the oligomers can be excited by TPA in the near-infrared region; 2) intersystem crossing is efficient, and the triplet excited states are long-lived (> 1 μs) and absorb strongly in the visible and near-infrared region; 3) the long-lived triplet excited states can be

populated efficiently by TPA; 4) optical limiting of nanosecond, near-infrared nanosecond pulses has been observed via the TPA/RSA mechanism. A selected set of results are presented below.

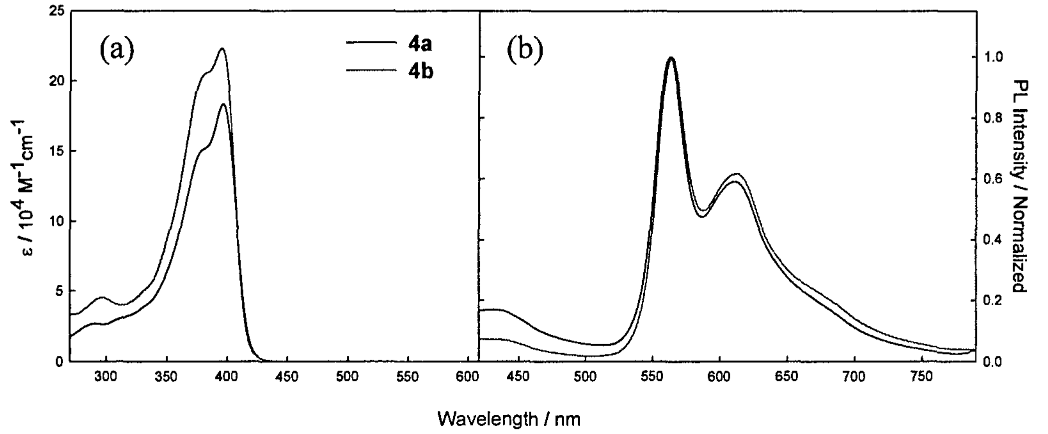


Figure 6. (a) Absorption spectra of **4a** and **4b** in THF solution. (b) Normalized photoluminescence spectra of **4a** and **4b** in deoxygenated THF solution resulting from excitation at 397 nm.

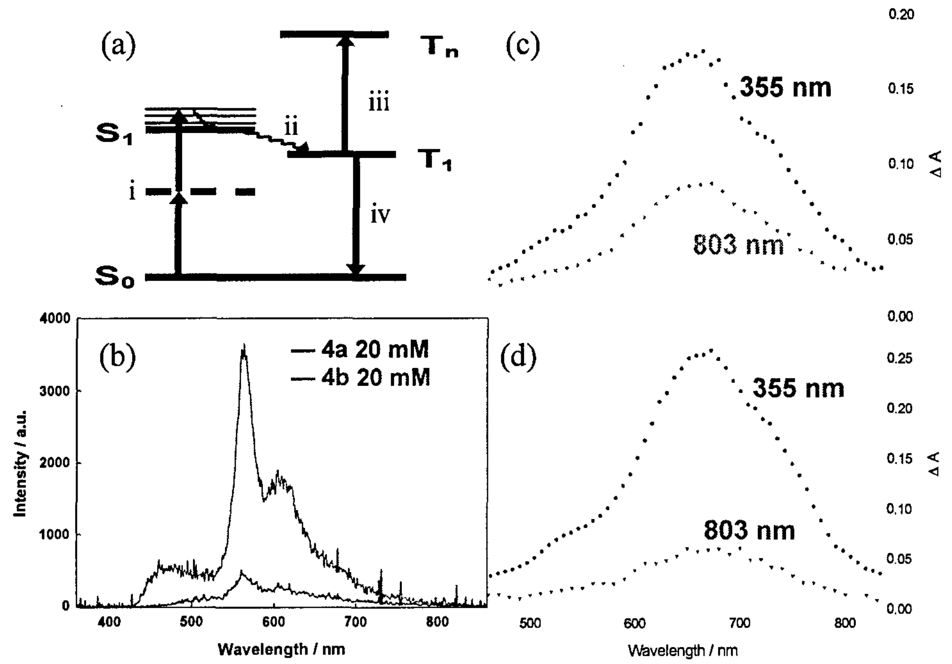


Figure 7. (a) Jablonski diagram illustrating: (i) two-photon absorption to the singlet excited state, (ii) intersystem crossing to the triplet excited state, (iii) triplet-state absorption, (iv) phosphorescence from relaxation of the triplet state to the ground state. (b) Emission of degassed 20-mM THF solutions of **4a** and **4b** resulting from pulsed excitation at 1064 nm. (c) Transient absorption difference spectra for **4a** following 355 nm excitation (blue) and 803 nm excitation (aqua). (d) Transient absorption difference spectra for **4b** following 355 nm excitation (red) and 803 nm excitation (magenta).

The one-photon absorption and one-photon excited photoluminescence spectra of the Pt(II) oligomers **4a** and **4b** are shown in Figure 6. The spectra of the two oligomers are nearly identical, indicating that the absorption in both oligomers is dominated by a π,π^* transition localized on the π-conjugated "ligand". Both complexes exhibit strong phosphorescence at λ_{max} = 563 nm and weak fluorescence at $\approx$ 400 nm. The intersystem crossing yields and phosphorescence efficiency of both complexes are *ca.* 0.9 and 0.5, respectively, which demonstrates the strong influence of spin-orbit coupling of Pt on enhancing the triplet yield and radiative decay from the triplet state. Both of these processes are spin-forbidden, and have considerably lower efficiency in the unmetallated π-conjugated "free ligands".

Figure 7 summarizes the results of two-photon excited photophysics for **4a** and **4b**. First, the photoluminescence of the two complexes produced by 10 ns pulsed, 1064 nm excitation (Fig. 7b) is the same as that observed under low intensity (one-photon) excitation. This emission is believed to arise by a sequence involving two-photon absorption to produce the singlet excited state, intersystem crossing to produce the triplet state, and phosphorescence (paths i, ii and iv Fig. 6a). Even more interesting is that as shown in Figure 7c and 7d, the transient absorption of the triplet excited state can be observed for one-photon excitation (355 nm) *and* two-photon excitation (803 nm). The fact that strong absorption is seen for the triplet state under two-photon excitation conditions clearly indicates that a relatively large excited state population of the triplet can be produced via TPA, even with a nanosecond pulsed laser.

A similar series of experiments was carried out on Ir(III) complex **5** (Scheme 4), and the data indicates for this complex it is also possible to efficiently populate a long-lived triplet state by two-photon excitation at 1064 nm. Specifically, as shown in Figure 8a, **5** exhibits a one-photon π,π^* absorption band at 500 nm and a weak phosphorescence band ($\phi_{em} \approx 0.003$) from the triplet state at 750 nm. The one-photon excited transient absorption spectrum of **5** (Fig. 8b) shows that the triplet excited state absorbs strongly throughout the visible and near-infrared regions, with $\lambda_{max} \approx 900$ nm and $\varepsilon_{max} \approx 3.2 \times 10^4$ $M^{-1}cm^{-1}$. As shown in Figure 9a and 9b, the phosphorescence of the triplet state can be produced by two-photon excitation at 1064 nm. Despite the fact that the phosphorescence efficiency for **5** is low, the phosphorescence can be observed by eye under 1064 nm, two-photon excitation (Fig. 9b), suggesting that near-infrared excitation affords a relatively high yield of the triplet state.

The experiments outlined above demonstrate that: 1) two-photon excitation of **5** at 1064 nm gives a high yield of the triplet state; 2) the triplet state has a strong near-infrared absorption ($\varepsilon_{1064\ nm} > 10^4$ $M^{-1}cm^{-1}$); 3) the ground state has negligible absorption at 1064 nm ($\varepsilon_{1064\ nm} < 1$ $M^{-1}cm^{-1}$). These conditions provide the basis for the observation of efficient non-linear absorption via the TPA/RSA mechanism, and in preliminary experiments we have demonstrated this point. Thus, as shown in Figure 9c solutions of **5** exhibit non-linear absorption for 10 ns, 1064 nm pulses with energy > 0.5 mJ (pulses focused with a 10 cm focal length lens, *ca.* 0.5 J-cm^{-2} fluence). Importantly, the non-linear absorption is believed to arise by the mechanism shown in Figure 5b, i.e., two-photon absorption followed by intersystem crossing and reverse saturable absorption.

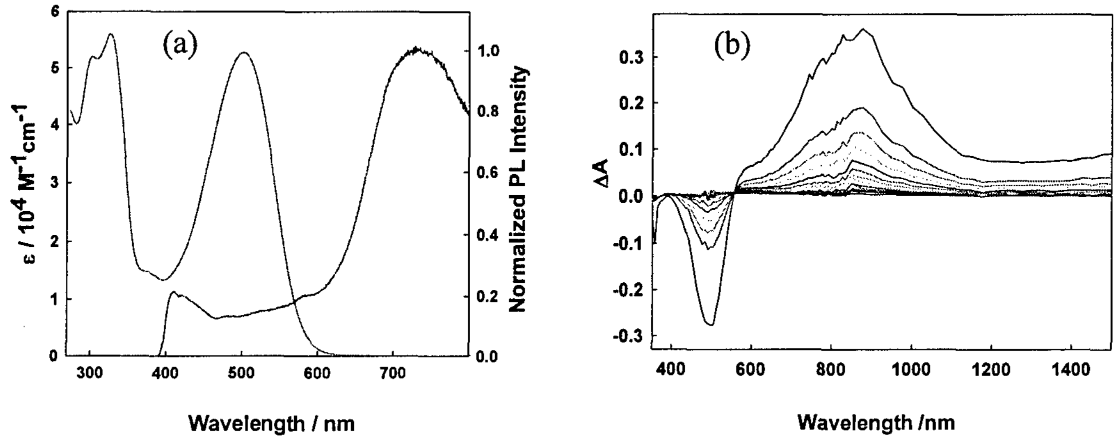


Figure 8. (a) Absorption (green) and emission spectra (red) of **5** in degassed THF solution. (b) Transient absorption difference spectra of **5** in degassed THF solution with 400 ns delay increments following 355 nm pulsed excitation.

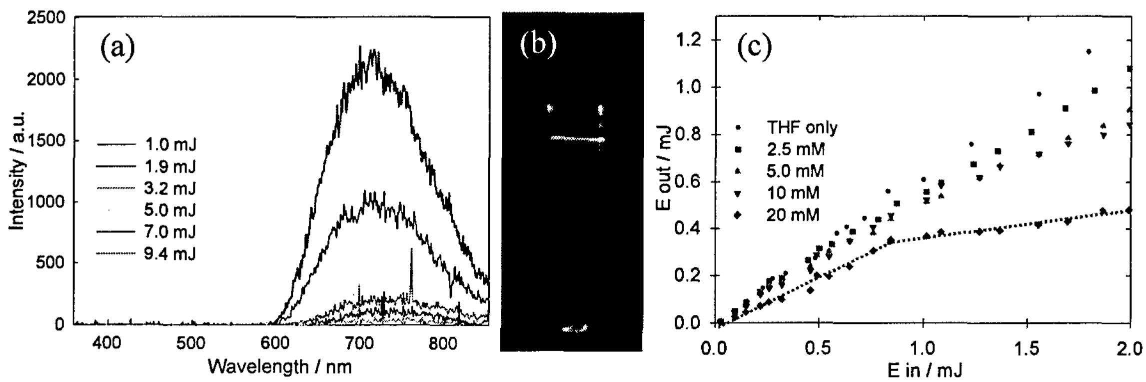


Figure 9. (a) Emission spectra of 5 mM **5** in THF solution following 1064 nm pulsed excitation at various energies. (b) Photograph of the visible emission from **5** excited by 1064 nm pulse. (c) Nonlinear transmittance of 1064 nm, 5 ns pulses for various concentrations of **5** in THF.

Taken together, the results of the work carried out on the organometallic TPA/RSA chromophores demonstrate that it is possible to produce long-lived triplet excited states in high yield by near-infrared TPA. Because the triplet excited states have large absorption cross sections, these molecular systems display non-linear absorption via the dual-mode TPA/RSA mechanism. It is evident that through the application of synthetic chemistry it will be possible to optimize the cross sections for TPA, and at the same time to tune the triplet-triplet absorption to give rise to chromophores that display efficient non-linear absorption for short and long laser pulses.

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Cumulative List of Personnel Contributing to Project : 2003 - 2006

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Kirk S. Schanze

Postdocs

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Kye-Young Kim: 2004 – 2006

Graduate Students

Richard Farley: 2003 – 2006
Thomas Cardolaccia: 2004-2005
John Peak: 2005-2006

Visiting Students:

Alexandre Hefele: 2005